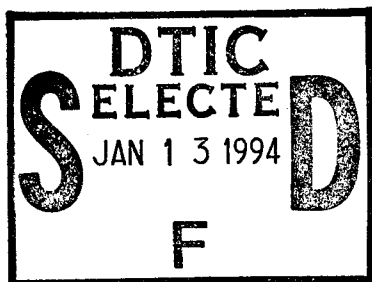


**Properties of New Materials Relevant to Energy and Fuel Research**



**Cleanthes A. Nicolaides**

**National Hellenic Research Foundation,  
Theoretical and Physical Chemistry Institute,  
48 Vas. Constantinou Ave., 116 35 Athens, Greece**

**AFOSR- 91- 0405**

**September 30, 1991 - June 29, 1994**

This document has been approved  
for public release and sale; its  
distribution is unlimited.

DTIC QUALITY INSPECTED 8

**19950112 049**

## REPORT DOCUMENTATION PAGE

FORM Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 1/12/94	3. REPORT TYPE AND DATES COVERED FINAL 30/9/91 - 29/6/94	
4. TITLE AND SUBTITLE Properties of New Materials Relevant to Energy and Fuel Research		5. FUNDING NUMBERS  AFOSR-94-0205	
6. AUTHOR(S)  Cleanthes A. Nicolaides			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Hellenic Research Foundation Theoretical and Physical Chemistry Institute 48, Vas. Constantinou Ave. Athens 11635 Greece		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) European Office of Aerospace Research and Development 223/231 Old Marylebone Rd., London NW1 5TH UK		10. SPONSORING/MONITORING AGENCY REPORT NUMBER  TR-95-01	
11. SUPPLEMENTARY NOTES			
12. DISTRIBUTION STATEMENT  Approved for public release Distribution unlimited		13. DISTRIBUTION STATEMENT  UNCLASSIFIED	
13. ABSTRACT (Maximum 200 words)  The work represents a contribution toward the quantitative understanding of certain energy trapping and release processes of the molecular level for novel compounds. In particular, it has dealt via advanced computations with questions of formation, properties as equilibrium and at transition states, and of spontaneous or laser-induced fragmentation of unusual molecules existing because of local minima on repulsive surfaces. Such molecules are a number of new nonclassical hydrogen complexes (E.g. OBeH <sub>2</sub> , F <sub>3</sub> AlH <sub>2</sub> , F <sub>4</sub> Mg <sub>2</sub> H <sub>2</sub> ). For diatomic volcanic and excimer states, newly developed ab initio computational methods were applied for obtaining the time-dependent probabilities for a number of multiphoton dissociation and excitation processes.			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT

TR-95-01

This report has been reviewed and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.



OSAMA ELBAYOUMI, Ph.D.  
Chief, Chemistry



DONALD R. ERBSCHLOE, Lt Col, USAF  
Chief, International Programs

Accession For		1
NTIS	CRA&I	<input checked="" type="checkbox"/>
DTIC	TAB	<input type="checkbox"/>
Unannounced		<input type="checkbox"/>
Justification .....		
By .....		
Distribution /		
Availability Codes		
Dist	Avail and/or Special	
A-1		

TR-95-01

Project title: "Properties of New Materials Relevant to Energy and Fuel Research"

Grantee: Cleanthes A. Nicolaides  
National Hellenic Research Foundation,  
Theoretical and Physical Chemistry Institute,  
48, Vas. Constantinou Ave.,  
Athens 116 35, Greece

Grant: AFOSR-91-0405

**Final Technical Report (September 1991-July 1994)**

**Summary**

The work represents a contribution toward the quantitative understanding of certain energy trapping and release processes of the molecular level for novel compounds. In particular, it has dealt via advanced computations with questions of formation, properties as equilibrium and at transition states, and of spontaneous or laser-induced fragmentation of unusual molecules existing because of local minima on repulsive surfaces. Such molecules are a number of new nonclassical hydrogen complexes (E.g.  $\text{OBeH}_2$ ,  $\text{F}_3\text{AlH}_2$ ,  $\text{F}_4\text{Mg}_2\text{H}_2$ ). For diatomic volcanic and excimer states, newly developed ab initio computational methods were applied for obtaining the time-dependent probabilities for a number of multiphoton dissociation and excitation processes.

**"Properties of new materials relevant to energy and fuel research"**

**C.A. Nicolaides**

Our research activities were developed along two major directions (I and II below). The first was oriented toward the prediction, through concepts of chemical binding and reliable advanced computations, of new, nontransition metal-containing compounds capable of trapping hydrogen in molecular form. Examples of such molecules are the  $F_3AlH_2$  [1] and  $OBeH_2$  [2], which are formed in a local minimum of the ground potential energy hypersurface.

The second direction involved the development of theory and computational methods for the reliable solution of the time-dependent Schrödinger equation (TDSE), which is necessary for the rigorous study of processes of energy exchange induced by the interaction of short laser pulses with molecules [3-5]. Furthermore, we started the development of close-coupling scattering methods that can be used for the calculation of certain multichannel reaction problems involving volcanic states [6]. More specifically, what was accomplished and published is summarized below:

**I. Non-classical hydrogen complexes of nontransition metals.**

Two types of studies were carried out. The first dealt with the prototypical  $OBeH_2$  molecule [2], for which extensive calculations were carried out on the ground state potential energy surface in order to locate its isomers, the local and global minima of this surface, their energetics and the possible reaction paths going from one to the others.

All calculations were performed using state-of-the-art analytic gradient and geometry optimization techniques. The basis sets employed were judiciously chosen, based on wide experience gained by similar calculations on other molecules, to be large enough to provide reliable energetics and small enough to allow the project to be tractable. The level of theory was chosen to be that of the Fermi-Sea-multiconfiguration-self-consistent-field approximation, a level of theory ideally suited for this type of calculation.

The mapping of this PES, carried out over a period of several months and leading to results which provide insight into the workings of intramolecular rearrangements,

showed the existence of five isomers (or minima) on this surface, namely, on order of increasing energy, H-O-Be-H,  $\text{H}_2\text{O}+\text{Be}$ ,  $\text{OBeH}_2$ . It was shown that trapping of molecular hydrogen by BeO to form  $\text{OBeH}_2$  is possible and *barrierless*, but only if the  $\text{H}_2$  approaches BeO at right angles. Should this happen, it was also shown that this local minimum is stable enough to exist. The most interesting finding, however, was that from  $\text{OBeH}_2$  one can only go to the global minimum of the surface, i.e. H-O-Be-H, thus releasing a considerable amount of energy (more than 70 Kcal/mole).

The second series of studies involved the prediction of the existence (or nonexistence) and of properties of complexes involving light metal atoms and  $\text{H}_2$  in molecular form [1,7].

The technique of Moller-Plesset Perturbation Theory to second order was used, in conjunction with fully analytic gradient and second derivative methods. Location of stationary points was done with no constraints on the internal geometrical parameters other than symmetry where applicable, and the stationary points were characterized via full vibrational analysis in order to verify that the structures of interest correspond to true local or global minima of the potential energy surface.

Following the initial results on alkaline earth  $-\text{H}_2$  cations, [8], the possible structures  $\text{AlH}_2^+$ ,  $\text{AlH}_2^{2+}$  and  $\text{AlH}_2^{3+}$  were investigated.  $\text{AlH}_2^{2+}$  is found to be a non-classical type complex with a binding energy of 20.6 kcal/mol.  $\text{AlH}_2^+$  is also similar, but extremely weakly bound. The search for a complex containing two metal atoms bound by a metal-metal bond on the other hand, reveals that no stable  $\text{Al}_2\text{H}_4^{2+}$  structure exists in the gas phase, contrary to  $\text{B}_2\text{H}_4^{2+}$  which is a stable classical hydride.

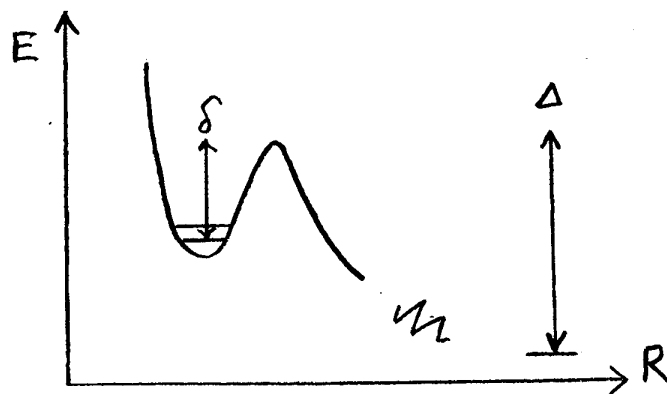
As regards the research for neutral  $\text{H}_2$  complexes, extensive calculations were performed in order to locate complexes of magnesium and aluminum fluorides. A planar  $\text{C}_{2v}$   $\text{F}_2\text{Mg}\dots\text{H}_2$  and an eclipsed  $\text{C}_s$   $\text{F}_3\text{Al}\dots\text{H}_2$  structure were found to be stable structures in the gas phase, by about 2.4 and 2.7 kcal/mol respectively (at the MP2 level of theory), when all corrections due to basis set superposition error (BSSE) are taken into account. In both cases,  $\text{H}_2$  retains its molecular nature to a great extent, the red shifts in the H-H harmonic stretching frequency being 137 and 120  $\text{cm}^{-1}$  respectively. Full structural and vibrational analysis was performed on both complexes, providing useful predictions to facilitate the experiment detection and characterization.

High quality computations were also performed on the dimer  $\text{Al}_2\text{F}_6$ , for which the theoretical investigations reported in the literature are extremely approximate and very few experimental data have been published. Preliminary investigations however, using analytic gradient methods, did not reveal the existence of any  $\text{H}_2$  complexes with this dimer.

Finally, magnesium fluoride dimers ( $\text{Mg}_2\text{F}_4$ ) and their  $\text{H}_2$  complexes were studied. Two stable forms were found, having  $D_{2h}$  and  $C_{3v}$  symmetries, for which the harmonic vibrational and infrared intensities were calculated [7].

## II. Laser pulse induced multiphoton dissociation of volcanic states.

Molecules which exist in local minima on overall repulsive surfaces can produce excess energy upon bond breaking. This can be seen from the plot below, representing a one-dimensional section of the "volcanic" hypersurface of such molecules or a diatomic molecule.



The break-up energy which is required ( $\delta$ ) is smaller than that which is released ( $\Delta$ ).

A technologically practical way to induce such fragmentation, is to expose molecules to strong laser pulses of IR frequency. In order to study this phenomenon rigorously, we developed a general ab initio method for solving the corresponding TDSE [3]. Applications have thus far been made to  $\text{BeH}^{++}$  [3] and  $\text{NO}^{++}$  [4], both of which have volcanic ground state potentials. In the study of  $\text{BeH}^{++}$  interacting with a laser pulse, the intensity was in the range  $10^{10}$ - $10^{11}$  W/cm<sup>2</sup>, the frequency that of the  $\text{CO}_2$  lasers and the duration 0.44 ps. In spite of the relatively low intensities, the known phenomenon of above threshold dissociation (ATD) was obtained, as well as a new one, which we named below threshold dissociation (BTD), since it requires fewer photons than expected from energy considerations. The reason for these results is the volcanic shape of the potential energy of  $\text{BeH}^{++}$ , which supports a relatively small number of vibrational quasi-discrete levels, of which the two near the barrier top mix heavily with the adjacent dissociation continuum. On the other hand, in  $\text{NO}^{++}$  [4], both the lowest two states ( $X^2\Sigma^+$  and  $A^2\Pi$ ) exist in local minima and offer a real model of low-lying embedded vibrational spectra, where both the discrete and the continuous parts couple via the electric dipole interaction. It was found that this coupling enhances the dissocia-

tion through the  $A^2\Pi$  state, which controls the dynamics of the dissociation.

Finally, the possibility of solving ab initio the TDSE for real systems gave us the opportunity of computing for the first time the formation of excimer states of noble gas hydrides ( $HeH$ ,  $NeH$ ,  $ArH$ ), and of  $HeF$ , by absorption of femtosecond pulses from the repulsive ground states [5]. Additional information was obtained regarding energy transfer processes in these excited states. For example, starting the photoreaction in  $HeF$  from the first excited repulsive state  $1^2\Pi$  with a pulse of frequency 4eV, allows an experimentally verifiable probability of obtaining bound-continuum emission at about 1320 Å (9.4 eV).

In conclusion, considerable progress was made during this project (see reference list) in the development of advanced theory and computational methods and in the ab initio understanding of certain materials and processes related to energy storage, release and transfer at the molecular level, taking into account the interaction with pulsed lasers as well. Our efforts adhered to the original research objectives but also expanded into the rapidly developing field of time-dependent pulsed laser induced molecular dissociation.

Some of this work was presented in lectures at Universities and Laboratories of Europe and the USA, (including Los Alamos and the Florida Solar Energy Center), and at International meetings. Finally, the grant allowed the partial support of my research associates Drs. Mercouris, Petsalakis, Simandiras and Valtazanos.

#### References

1. C.A. Nicolaides and E.D. Simandiras, Chem.Phys.Lett. 196 213 (1992).
2. P. Valtazanos and C.A. Nicolaides, J.Chem.Phys. 98 549 (1993).
3. C.A. Nicolaides, Th. Mercouris and I.D. Petsalakis, Chem.Phys.Lett. 212 685 (1993).
4. Th. Mercouris, I.D. Petsalakis, P.Valtazanos and C.A. Nicolaides, J.Phys. B27 L519 (1994).
5. I.D. Petsalakis, Th. Mercouris and C.A. Nicolaides, Chem.Phys. 189 (1994).
6. A. Vegiri and C.A.Nicolaides, "Close-coupled calculations of multichannel resonances in molecules", unpublished, (1994).
7. E.D. Simandiras and C.A. Nicolaides, Chem.Phys.Lett. 223 233 (1994).
8. E.D. Simandiras and C.A. Nicolaides, Chem.Phys.Lett. 185 529 (1991).